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Low Temperature Epitaxial Growth of Rare Earth Doped Silicon and Silicon Germanium Alloys

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13. ABSTRACT (*Maximum 200 words*)

PL and EL from a forward biased PN junction have been observed from Er doped Si produced in this investigation. The material was deposited epitaxially in a low temperature process (500 °C) involving PECVD using an ECR source. The dopant source was a metal organic compound, tris (bis trimethyl silyl amido) Er (III), which contained three nitrogen atoms bonded directly to Er. This bonding arrangement was beneficial in forming an intact, optically active center in the epitaxial Si material. The metal organic dopant precursor used however contained 18 C atom which to a large extent also became incorporated in the deposited film. Attempts to operate the fabricated PN junctions in reverse bias breakdown failed due to excessive leakage in the material caused by the high level of carbon impurities.

Later work shifted to growing the epitaxial layer doped with only Er, with no co-dopants to improve the electrical transport properties of the material. This would also answer some basic physical questions about the role of co-dopants in the emission properties of the Er center. This was accomplished by adding an Er sputter gun to the reactor, and operating it during the PECVD growth of Si. We are still in the process of getting some of the bugs out of this process but we see no physical reason why it should not yield significant reverse bias EL.

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concerning the

LOW TEMPERATURE EPITAXIAL GROWTH OF RARE EARTH DOPED SILICON AND SILICON GERMANIUM ALLOYS

Grant Numbers F49620-94-1-0427

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A. Publications

1. J. L. Rogers, P. Andry, W. J. Varhue, P. McGaughnea, Ed Adams, R. Contra, "Low temperature homoepitaxial growth of Si by ECR-PECVD", 67 (7) 1995.

2. J. L. Rogers, P. S. Andry, W. J. Varhue, E. Adams, M. Lavoie and P. B. Klein, "Erbium Doped Silicon Films Grown by Plasma Enhanced Chemical Vapor Deposition", Journal of Applied Physics 78 (10) 6241 (1995).

4. P. Andry, J. L. Rogers, W. J. Varhue, E. Adams, M. Lavoie, P. Klein, R. Hengehold, and J. Hunter, "Growth of Er-doped Si using Metal Organic Dopant Sources", Presentation at the American Vacuum Society in Minneapolis. (Oct 1995).

3. W. J. Varhue, J. L. Rogers, P. Andry, and E. Adams, "Epitaxial Film Thickness in the Low Temperature Growth of Si(100) by Plasma Enhanced Chemical Vapor Deposition", Appl. Phys. Lett. 68 (3) 349 (1996).

4. P. Andry, J. L. Rogers, W. J. Varhue, E. Adams, M. Lavoie, P. Klein, R. Hengehold, and J. Hunter, "Growth of Er-doped Si using Metal Organic Dopant Sources", Presentation at the American Vacuum Society in Minneapolis. (Oct 1995).

5. P. S. Andry, W. J. Varhue, F. G. Anderson, E. Adams, M. Lavoie, P.B. Klien, R. Hengehold and J. Hunter, "Low Temperature Growth of Si:Er by Electron Cyclotron Resonance PECVD Using Metalorganics", Mater. Res. Soc. , San Fransisco, 422 57 (1996).

6. P. S. Andry, W. J. Varhue, F. Ladipo, K. Ahmed, E. Adams, M. Lavoie, P.B. Klien, R. Hengehold and J. Hunter, " Growth of Er-doped Si using Metalorganics by Plasma Enhanced Chemical Vapor Deposition", J. of Applied Physics, 80 (1) 551 (1996).

7. W. J. Varhue, J. L. Rogers, P. S. Andry, E. Adams, M. Lavoie and R. Kontra, "Low Temperature Deposition of Epitaxial Si", Solid State Tech. , 163 June (1996)

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Introduction

This document is the final technical report on the LOW TEMPERATURE EPITAXIAL GROWTH OF RARE EARTH DOPED SILICON AND SILICON GERMANIUM ALLOYS under Award #F49620-94-1-0427. The concept of Er doped semiconductors presents an exciting prospect for the potential development of Si based optoelectronics technology. In the past 5-6 years, there has been a widespread effort to obtain efficient optical emission from Er doped Si. To date however, the level of recorded emission has been weak. In retrospect it is possible that a majority of this effort was in vain in that efficient luminescence was sought from an exciton or electron-hole pair (EHP) mediated processes. Photoluminescence(PL) and electroluminescence(EL) from a forward biased junction are both such processes. In photoluminescence the exciton is formed by the absorption of light. Studying it was more convenient than EL from a forward biased junction as that would have required the fabrication of a diode structure. Once formed the exciton could migrate through the material and ideally transfer its energy to the Er metal ion. We believe that what has been largely studied in these investigations has been the efficiency of energy transfer from the exciton to the Er ion complex. The efficiency of this transfer has been found to be dependent on the temperature of the semiconductor host, the concentration of free carriers in the host (doping level), and the microenvironment of the Er impurity(co-dopants). The dependence on temperature results from the thermal destruction of the exciton at anything other than very low temperatures, > -50 K. The high concentration of free carriers, doping level, causes the loss of the free exciton through recombination and thus no Er emission. Finally, the presence of co-dopant atoms; C, N, O and F, with the Er metal impurity was found to be essential to obtain a reasonable PL signal. It was shown that the co-dopant atoms formed a cage around the Er metal ion impurity. Theories explaining the purpose of this cage include the concept that these perturbations cause a mixing of the electron orbitals which then permit transitions in a previously parity forbidden process.

One of my colleagues, Prof. Frederick Anderson at the University of Vermont was the first to propose that the role of the co-dopants was to form a phonon cage around the Er metal ion. Free excitons once formed diffuse through the Si lattice and may become bound to the Er metal impurity. The suspicion at this point is that these bound excitons are shielded from the bath of phonons that exist in the Si lattice by this low mass ligand cage. Without a proper ligand cage, efficient PL or EL from a forward biased PN junction for Er doped Si

would not be possible. The goal of most investigations as well as our own became an effort to design and produce material with the best co-dopant cage, which would yield the highest signal from an exciton mediated process.

In 1997, Stimmer et. al. reported the room temperature emission of 1.54 micron light from a reverse biased diode. In this process it is assumed that the Er ion is excited directly by impact excitation by hot electron. The exact nature of this excitation process remains somewhat unclear and additional work is called for. These investigators and several others that followed, have constructed reverse biased diodes made with Si, doped with Er and co-dopants. Their method to produce the semiconductor starting material was by ion implantation or molecular beam epitaxy, creating a dopant mixture of Er and proven co-dopants; O, N, and B. We have also attempted to construct and operate diodes working in the reverse biased condition but have had poor results. We have concluded that high crystalline quality material is essential to successfully operate a diode in reverse bias with a high breakdown field. The inclusion of a high concentration of co-dopant atoms is not favorable to the production of high crystalline quality material. In our process, to grow epitaxial Si with an Er doping concentration of 10^{19} atoms/cm^3, both wanted and unwanted co-dopants were included. The wanted co-dopants in our case were three nitrogen atoms per Er atom, believed to be bonded to the Er atom. The unwanted co-dopants in our particular process were that of carbon, remanants of the metal organic precursor. The addition of these large concentrations of impurities undoubtedly produced excessive defects in the material. The high defect density reduced the mean free path of free carriers, and resulted in a large leakage current. With such material it was not possible to to sustain reverse bias fields sufficient to produce electron energies capable to cause impact ionization in the material.

Although all published work on the emission of light from reverse biased junctions has involved the use of Er doped material with co-dopants, we have come to question the need for co-dopants. In the exciton mediated process, the role of the co-dopants is we believe to isolate the Er ion/ exciton assembly from the phonon bath that exists in the Si lattice. The true question is, if the Er ion is directly excited by electron impact can it de-excite through a phonon initiated process. If it cannot, then the presence of co-dopants is perhaps not necessary, and from an electron transport point of view totally unwanted.

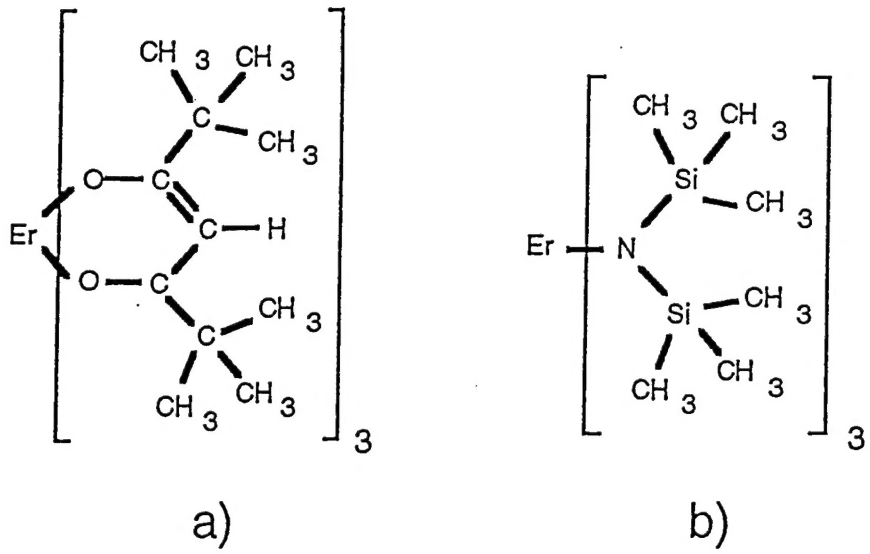
Once confronted with these results and conclusions, we have made every attempt and continue to do so today, despite the lack of

financial support, to perfect our process to produce the highest quality epitaxial Si with a high concentration of pure Er impurities. We have modified our growth chamber to include an Er metal sputter source, with shutter, to permit the incorporation of Er atoms without co-dopants. In a further effort to improve crystal quality we have changed our previous substrate heating system which relied on bare W filaments, to a new BN encased pyrolitic graphite heater. All the changes are in place and we are growing and characterizing material to obtain the optimum operating conditions.

Results

Although we have come to the above conclusions, the work performed under this contract was as successful as that of other investigators at obtaining both PL and EL from forward biased PN junctions. All the results present here reflect measurements made on material and devices fabricated in our lab. The process investigated here relied on the low temperature (<500 C) epitaxial growth of Si by plasma enhanced chemical vapor deposition (PECVD). The PECVD process used here, to be more specific, relied on the use of an electron cyclotron resonance(ECR) downstream plasma stream source. The Er dopant source was a metal organic compound that was sublimed into the reactor chamber through a gas shower located in front of the substrate. The metal organic precursor, tris (bis trimethyl silyl amido) Er (III), from now on referred to as "amido", was synthesized here at the University of Vermont by Prof. Kazi Ahmed, who original before his departure from UVM was a co-PI on this research contract. This metal organic precursor, the "amido", sketched in Figure 1 contained 18 carbon atoms as well as the three nitrogen atoms that bonded directly to the Er center. Use of this compound represented a vast improvement over the compound previously used, tris (2,2,6,6)-tetramethyl-3,5-heptanedionato erbium. Analysis of the samples by secondary ion mass spectrometry (SIMS) analysis did indicate that the deposited film contained a high concentration of carbon impurity, 10^{19} cm^{-3}.

Although we did come to the conclusion that the incorporation of some carbon impurity was beneficial in that it compensated for the incorporation of the larger Er impurity, the level obtained was excessive. Erbium and its ligand structure would shift the x-ray peak in a direction indicative of an expansion of the crystal lattice, whereas carbon incorporation shifted the peak back in the opposite direction. This maybe an indication for future work, in that the incorporation of a small amount of carbon may be beneficial in



a) b)

Figure 1. Molecular structure of MO dopants, a) tris (2,2,6,6-tetramethyl-3-5-heptanedionato) Er (III) and b) tris (bis trimethyl silyl amido) Er (III)

relieving the compressive strain caused by the incorporation of the larger Er or Er ligand structure.

An example of the photoluminescence emission spectrum for a epitaxially grown Si sample doped with the "amido" Er source is shown in Figure 2. The fine structure contained in this spectrum was sufficient for theorist, namely Dr. Frederick Anderson, to formulate a model describing the observed transitions. The photoluminescence emission intensity of this material has been compared with that obtained by other US research groups, by characterizing these samples in our photoluminescence facility at UVM. The material prepared in the UVM reactor is comparable in intensity to the best material currently being produced by these other groups. The Si material has been doped with Er at concentrations exceeding 1 x 10^{20} cm^{-3}.

In a separate effort, work was also performed on the *in-situ* doping of Si thin film material during growth with Sb using a sputter gun located in the ECR reactor. This technique has been used to make reasonable quality PN junctions.

Fabrication of p-Si:Er-n Junctions

The expertise gained in doping silicon, both with the amido or ErN_3 complex to produce luminescence, and with Sb to create an electrical junction, has been combined in this effort to fabricate LED devices. A series of depositions were performed using both 20 ohm-cm p^- and 0.005 ohm-cm p^+ substrates, where the bulk of the film, 5,000 Å, was amido-doped and the upper 500 to 700 Å was Sb-doped. All such double-layered films were analyzed by x-ray diffraction to assure good epitaxial quality. Two of the best results from the EL growth series are reported in Table 1.0. Growth parameters for both samples were: 480°C substrate temperature, 5 mTorr pressure, 5.0 sccm silane flow (50 sccm total x 10%) and 7.5 W rf sputtering power to the Sb target in the last 15 minutes.

Table 1.0 Growth parameters and XRD characteristics for high quality epitaxial Si:Er / Sb-doped films grown on p-type substrates.

Sample	Substrate Thickness (Ω-cm)	ECR power (W)	(004) shift (Å/min.)	(Å)	Dep. rate FWHM (arcsec)	(arcsec)
PA210	0.005	250	47	4000	+135	70
PA217	20	200	33	4000	+116	50

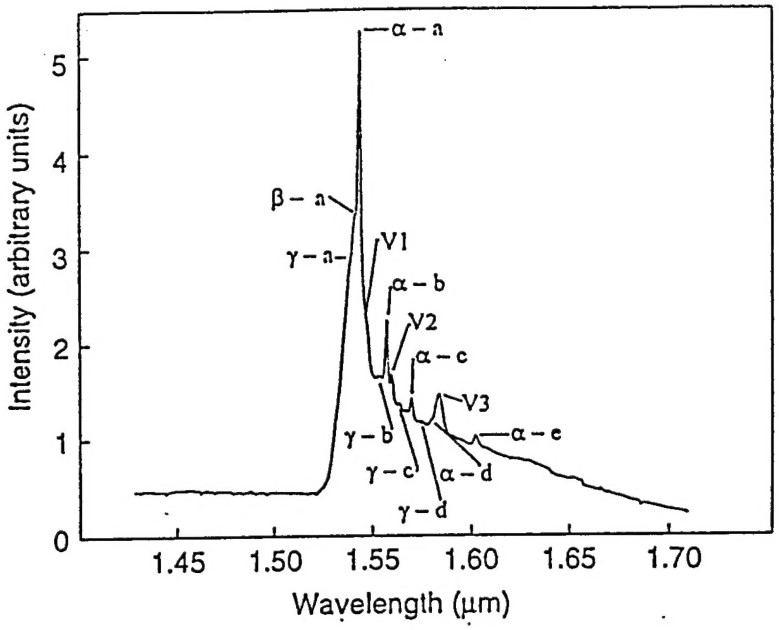


Figure 2. Current best photoluminescence spectrum from unannealed sample showing fine line structure.

The IV characteristics of the PA217 mesa under forward and reverse bias are shown in Fig. 3.0. Note the difference between the forward bias curves at room temperature and 200 K. For a given current at 295 K, an additional +3 V is required to achieve the same magnitude at 200 K. The reverse bias curves are separated from their forward bias counterparts by roughly 3 orders of magnitude, and reach values on the order of tenths of a milliamp. The inclusion of the Si:Er layer appears to introduce a significant density of electronic defects to the device which multiplies leakage current by several orders of magnitude. None of the mesas probed on sample PA217 exhibited reverse breakdown, even at bias levels as high as -50 volts.

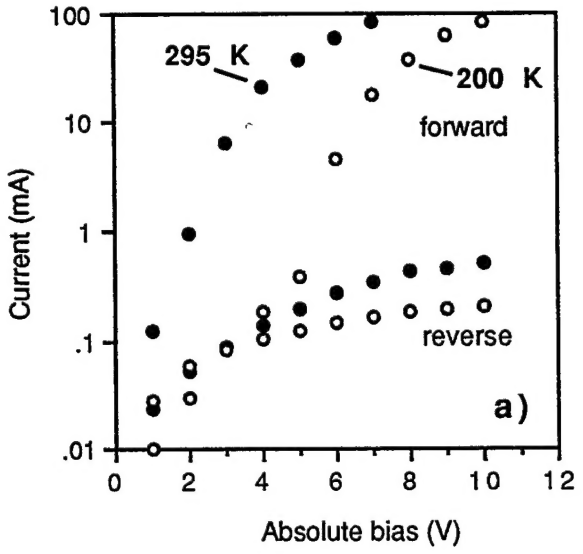


Figure 3.0 IV plots for PA217 mesa under forward and reverse bias at room temperature and 200 K.

The luminescent output of PA217 mesa as a function of forward bias current at room temperature, 250 K and 200 K is shown in Fig. 4.0. The output power was measured using a Ge optical power sensor placed directly in contact with the cryostat window. While the output is only a few nW, there is clearly an increase as the temperature is reduced. Below 200 K, contact problems developed preventing measurement of either currents or EL powers. This is particularly disappointing as previous PL quenching measurements have showed that luminescence virtually disappears at temperatures above 150 K.

For the mesa geometry used here, a current of 100 mA corresponds to a current density of 1.4 A/cm^2.

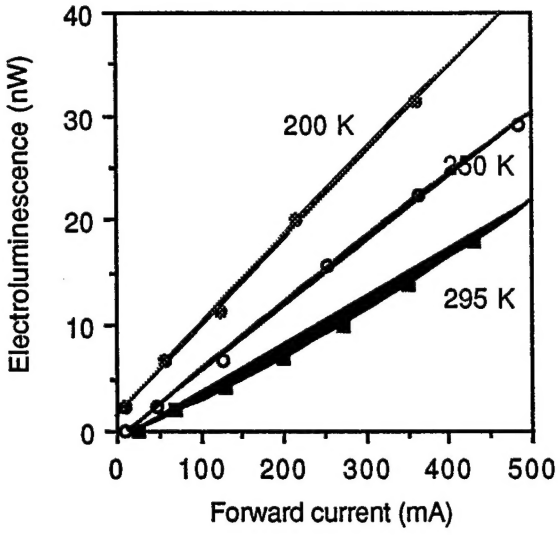


Figure 4.0 Electroluminescent output of PA217 mesa as a function of forward bias current for three different temperatures.

The ultimate goal of this research effort is to produce a room temperature EL junction, and samples such as PA210 were produced with this in mind. These were deposited on degenerately doped p-type substrates with the intention of running them in the reverse bias breakdown regime. This is based on the notion that thermal quenching observed in both PL studies and forward biased EL junctions can be overcome if the Er atoms are excited by another mechanism such as electron impact ionization. The room temperature IV curve for the PA210 mesa is shown in Fig. 5.0. The reverse bias behavior of the device with its rounded downward curve indicates significant tunnel current. From the figure, a current density of ~11 A/cm^2 is indicated at a reverse bias of -7 V. The shape of this IV curve, as well as the current densities and bias range, are remarkably similar to the room temperature EL junctions grown using MBE by Stimmer *et al.* [1]

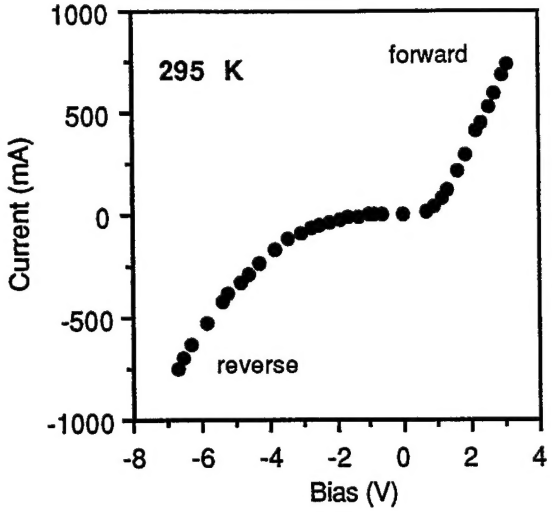


Figure 5.0 Room temperature IV curve for sample PA210 mesa under forward and reverse bias.

To date, room temperature EL has been limited to no more than a few nW from samples such as PA210, even at reverse bias current densities of more than 10 A/cm^2. At these injection levels, ~5 W were dropped across the 3 mm diameter device and significant heating resulted. Pulsed operation would most likely give results similar to that of Stimmer *et al.* [1] who have reported a reasonable EL signal when their devices were pulsed using a 10:1 duty cycle.

Our present thinking is that light emission is limited by electron scattering in the Er doped region. In otherwords, the crystal quality of the Er doped Si region is not adequate to give a mean free path long enough for the electrons to gain sufficient energy to excite the Er centers. The poor crystal quality is a direct result of our process that incorporates a large concentration of carbon through the use of the metal organic dopant sources. Other groups have shown that carbon co-doping is beneficial in obtaining a reasonable PL signal, however in this case the addition is uncontrolled and excessive.

In light of these shortcomings, we have abandoned the use of metal organic dopant sources and are currently using an in-situ Rf sputter gun with a pure metallic sputter target. The incorporation of Er has been found to shift the xray spectrum film in a direction indicating an increase in lattice constant. Future plans include the incorporation of carbon through the use of methane feed gas to shrink the lattice constant and match the underlying Si substrate. This is very similar to the current work that uses the SiGeC ternary alloy to grow lattice matched epitaxial layers on Si substrates. In

theory this material should be produced with a low density of defects and therefore should result in a long electron mean free path that supports a significant breakdown current density.

Other Device Structures

We have also been experimenting with other device structures to obtain efficient light emission from an impact ionization source. Two of these structure have included a bipolar junction and a metal junction field effect transistor design. To date we have not obtained reasonable emission from these devices. The for the as yet poor results has been to inability to obtain reasonable quality Er doped epitaxial Si. We had made several changes to our epitaxial system; including substrate heater, in-situ sputtering system

1. J. Stimmer, A. Reittinger, J. F. Nutzel, G. Abstreiter, H. Holzbrecher and C. Buchal, Appl. Phys. Lett. 68 3290 (1996).